

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
30 September 2004 (30.09.2004)

PCT

(10) International Publication Number
WO 2004/083138 A1

(51) International Patent Classification⁷: **C03B 19/12**

(21) International Application Number:
PCT/EP2004/002578

(22) International Filing Date: 12 March 2004 (12.03.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
NO 2003 A 000006 21 March 2003 (21.03.2003) IT

(71) Applicant (for all designated States except US): NOVARA TECHNOLOGY S.R.L. [IT/IT]; Via Fauser, 4, I-28100 Novara (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BOARA, Giulio [IT/IT]; Via Moloise, 16, I-26013 Crema (IT). PEDRETTI, Simone [IT/IT]; Via San Giovanni, 105, I-28047 Oleggio (IT). RÜCKEMANN, Andreas [DE/IT]; Via Vecchia Circonvallazione, 5L, I-28047 Oleggio (IT). SPARPAGLIONE, Massimo [IT/IT]; Via Gorizia, 1, I-20097 S. Donato Milanese (IT).

(74) Agents: WEBER, Wolfgang et al.; European Patent Attorney, c/o Degussa AG, Intellectual Property Management, Postfach 13 45, 63403 Hanau (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR).

Declaration under Rule 4.17:

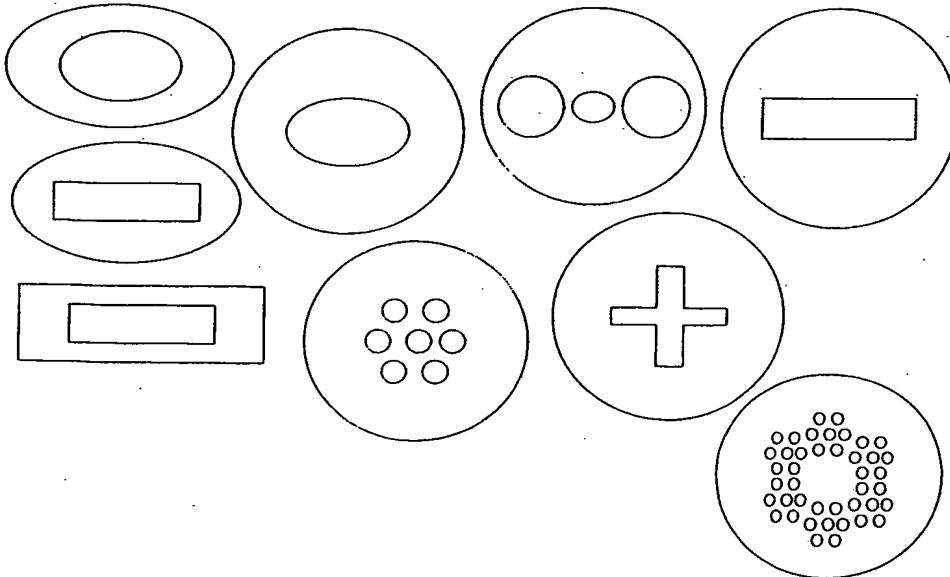
— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

{Continued on next page}

(54) Title: SILICON OXIDE BASED ARTICLES



(57) Abstract: Particularly shaped articles constituted by silicon oxide, as such or with suitable additives, prepared by room temperature molding according to a process comprising: preparation of a sol starting from a silicon alcooxide, or from a silicon alcoxide and at least a precursor of at least one of the additional elements; hydrolysis of the sol obtained thereby; addition of colloidal silica; pouring the resulting mixture into the desired mould; sol gelling and fast removal of the solid product; gel drying; gel densification by means of a thermal treatment at temperature ranging from 900 °C to 1500 °C. The articles can be used as preforms for the optical fiber spinning.

WO 2004/083138 A1



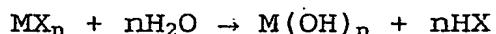
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

2pects
JC20 Rec'd PCT/PTO 19 SEP 2005**Silicon oxide based articles**

The present invention relates to articles, characterized by particular shapes, constituted by silicon oxide as such or suitably added, and obtained by molding at room temperature 5 through sol-gel procedures. Particularly the present invention relates to articles having a shape which is obtained by means of suitable moulds employed within the route of a sol-gel procedure and selected on the ground of the aimed final use, such a shape allowing the same to be 10 utilized in many fields: of particular interest is the preparation of preforms cut out for optical fiber spinning.

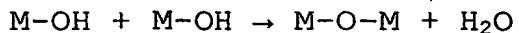
The sol-gel term defines a wide variety of processes which, even being different as far as the working details or the reagents are concerned, are characterized by the following 15 common operations:

- preparation of a solution, or a suspension, of a precursor formed by a compound of the element (M) the oxide of which has to constitute the final glassy article;
- 20 - hydrolysis, acid or base catalyzed, of the precursor, inside the solution or suspension, to form M-OH groups according to the reaction



wherein X generally is an alcohol residue and n means 25 the element M valence; the alcoxydes M(OR)_n can be replaced by soluble salts of the element M such as chlorides or nitrates, and, in some cases, oxydes. The obtained mixture, i.e. a solution or a colloidal suspension, is named sol;

- polycondensazion of the M-OH groups according to the reaction



which requires a time from few seconds to some days,
5 depending on the solution composition and the temperature; during the step, a matrix is formed called, case by case, alcohogel, hydrogel or more generally, gel;

- gel drying till the formation of a porous monolithic body; during this step, the solvent is removed through a simple controlled evaporation, which determines the so called xerogel, or through an extraction in autoclave which determines the so called aerogel; the obtained body is a porous glass, which may have an apparent density of 10% to about 50% of the theoric density of the oxide with the same composition; the dried gel can be industrially used as such;
- densification of the dried gel by a treatment at a temperature, generally ranging between 800°C and 20 1500°C, depending on the gel chemical composition and the preceding step process parameters; during this step the porous gel is becoming dense up to obtain a glassy or ceramic compact oxide having the theoric density, with a linear shrinkage equal to about 50%.

25 According to the above said 1a procedure, it is possible to prepare monoliths of the interesting material by pouring sol onto a suitable mould, or films too by pouring sol onto a suitable substrate, or preforms of optical fibers too.

With specific reference to these latter, it is known that 30 such fibers, largely employed in the telecommunication field, are constituted by a central portion, the so called "core", and by a couting around the core, generally named "mantle". A difference ranging about from 0,1% to 1%

tbetween the core and the mantle refraction indexes let light be confined in the core. Such a difference in the refraction index is obtained through different chemical composition of the core and the mantle.

5 Even if many combinations are evaluated, the most common is constituted by a glassy core formed by silicon oxide doped by germanium oxide ($\text{GeO}_2\text{-SiO}_2$) surrounded by a glassy SiO_2 mantle. The widest used optical fibers are of the monomodal kind, being characterized by one only allowed optical path.

10 10 Such fibers generally owns a core with a $4\text{-}8\mu\text{m}$ diameter and a mantle external diameter of $125\mu\text{m}$.

The most important parameter to evaluate the quality of a fiber is the relevant optical fading out, which is mainly due to light absorbing and diffusion mechanisms and is

15 measured in decibel for kilometer (dB/Km).

As the skilled people know, UV fading out is mainly due to the absorption by the cations (as the transition metal cations) present in the fiber core, while the IR fading out is mainly due to the absorption by -OH groups which may be

20 20 in the glass. The fading out of light having an intermediate wave length between UV and IR is mainly due to diffusion phenomena caused by fluctuations of the refraction indexes because of the glass unhomogeneity, of the fiber structure defects, such as imperfections in the

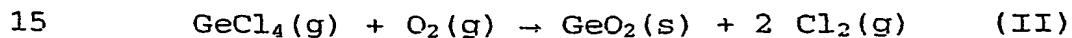
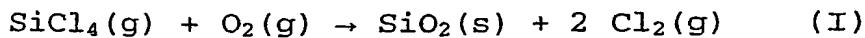
25 25 core-mantle contact surface, fiber bubbles or breaks, or impurities inglobed within the fiber during the production process.

The optical fiber are prepared by bringing a preform to temperatures of about 2200°C . The preform is an

30 30 intermediate in the fiber production, formed by an internal rod and an external coat corresponding to core and mantle of the final fiber. The ratio between the coating and rod diameters is equal to the one between the mantle and the core diameters in the finale fiber. Hereinafter, the words

rod and core will be respectively used with reference to the inner part of the preform and the final fiber, while the word mantle will be used to indicate the external part either of the preforms or of the fibers.

5 It is known that the mantle of the preforms for the commercially available optical fibers is produced according to modifications of the ground chemical deposition process from the vapor phase (better known as "Chemical Vapor Deposition" or the acronym "CVD"). All processes deriving
10 from CVD make generally use of gaseous mixtures comprising oxygen (O_2) and silicon chloride ($SiCl_4$) or germanium chloride ($GeCl_4$) into an oxy-hydrogen flame to produce SiO_2 and GeO_2 according to the reactions:



The oxydes produced thereby can be deposited as particles onto a cylinder carrier which is then removed or, as an alternative, onto the inner surface of a silica cylinder carrier which is then processed to form the mantle of the
20 final fiber.

The CVD based processes are suitable to produce optical fiber with 0,2 dB/Km minimum fading out (for transmitted light with 1,55 μm wave length), and are the state of the art in the field.

25 Even if these producing methods are quite satisfactory as to the performance of the resulting fibers, the yields are limited thus increasing the production costs.

It is also well known that, during the thermal treatments to achieve the complete densification of the dry gel, it is
30 possible to carry out chemical purification thereof. Through such treatments it is possible to take advantage from the dry gel porosity to carry out washing operations in the gaseous phase in order to remove organic impurities

caused to be present in the gel because of the organometallic precursors (as the previous mentioned TMOS and TEOS), as well as water, hydroxyl groups linked to the cations in the gel network, or undesired metal atoms.

5 Generally, the removal of organic impurities is obtained through a calcination carried out by flowing an oxidizing atmosphere (oxygen or air) into the dry gel at temperatures lower than 900°C, particularly between 350°C and 800°C.

10 The removal of water, hydroxyl groups and undesired metals is carried out by letting the gel pores be flowed by Cl₂, HCl or CCl₄, eventually mixtures with inert gases as nitrogen or helium, at temperatures between about 400°C and 800°C.

15 The last operation is usually a washing treatment, carried out with inert gases like nitrogen, helium or argon, to totally remove chlorine or chlorine containing gases from the gel pores. At the end of these treatments, gel is densified to the corresponding glass, totally dense (hereinafter such state will be designated also as "theoric 20 density") by heating at temperatures higher than 900°C, and usually higher than 1200°C, under a helium environment.

25 The above described treatments are quite suitable to purify gels so that the resulting glasses are suitable to be largely used (generally to build optical or mechanical parts). However, it has been found that these treatments cause the presence of gaseous compounds in the final glass. In case of processing the same in the temperature range of 1900 to 2200°C in order to draw the fibers, those gaseous compound traces give rise to microscopic bubbles which 30 become fracture starting points, thus causing the fiber to break and the known processes to be not suitable to produce optical fibers.

The present invention allows the preparation of preforms suitable to spin optical fibers without the above said drawbacks, such fibers having characteristics equal to and sometimes higher than the ones achievable by means of the
5 CVD technology. Moreover, the present invention relates to, according to a broad meaning, the preparation of articles having the shape desired in relation with the final use, constituted by silicon oxide, as such as suitably additivated, and comprising the above said optical fibers
10 preforms and, furtherly, liquid safety containers, transparent (and not) devices to be used in the chemical laboratories, vessels, and, more generally, vitreous products appointed at furnishing too.

Therefore, the present invention refers to particularly shaped articles constituted by silicon oxide, as such or suitably additivated, prepared by molding at room temperature according to the process comprising the following operations:

- preparation of a sol starting from a silicon alcoxide,
20 or from a silicon alcoxide and at least a precursor of at least one of the additional elements;
- hydrolysis of the sol obtained thereby;
- addition of colloidal silica;
- pouring the resulting mixture into the desired mould;
- 25 - sol gelling and fast removal of the solid product;
- gel drying;
- gel densification by means of a thermal treatment at temperature ranging from 900°C to 1500°C.

Preferred silicon alcoxides are tetramethylortosilicate and
30 tetraethylortosilicate. When one or more additives are to be added, the same are selected by the people skilled in

the art dependently upon the final purposes, the preferred one being chosen among the elements of the IIIa, IVa, Va, IIIb, IVb, Vb Groups of the Periodic Table. Even the mould will be selected by the people skilled in the art, again

5 dependently upon the aimed use of the final article.

Illustrative examples of the present invention, no way limiting the same, are the sections reported in figure 1 as to the optical fiber preforms, and in figure 2 as to some other possible employment.

10 In the above mentioned sol-gel procedure, all operations till the very molding are carried out at room temperature; the gel drying can be performed under ipercritical or subcritical conditions.

Claims

1. Particularly shaped articles constituted by silicon oxide, as such or suitably additivated, prepared by room temperature molding according to a process comprising:

- preparation of a sol starting from a silicon alcoxide, or from a silicon alcoxide and at least a precursor of at least one of the additional elements;
- hydrolysis of the sol obtained thereby;
- addition of colloidal silica;
- pouring the resulting mixture into the desired mould;
- sol gelling and fast removal of the solid product;
- gel drying;
- gel densification by means of a thermal treatment at temperature ranging from 900°C to 1500°C.

2. Articles according to the preceding claim to be used as preforms for the optical fiber spinning.

3. Articles according to claim 2 characterized by a shape having a section selected from the ones reported in figure 1.

4. Articles according to claim 2 characterized by a shape selected from the ones reported in figure 2.

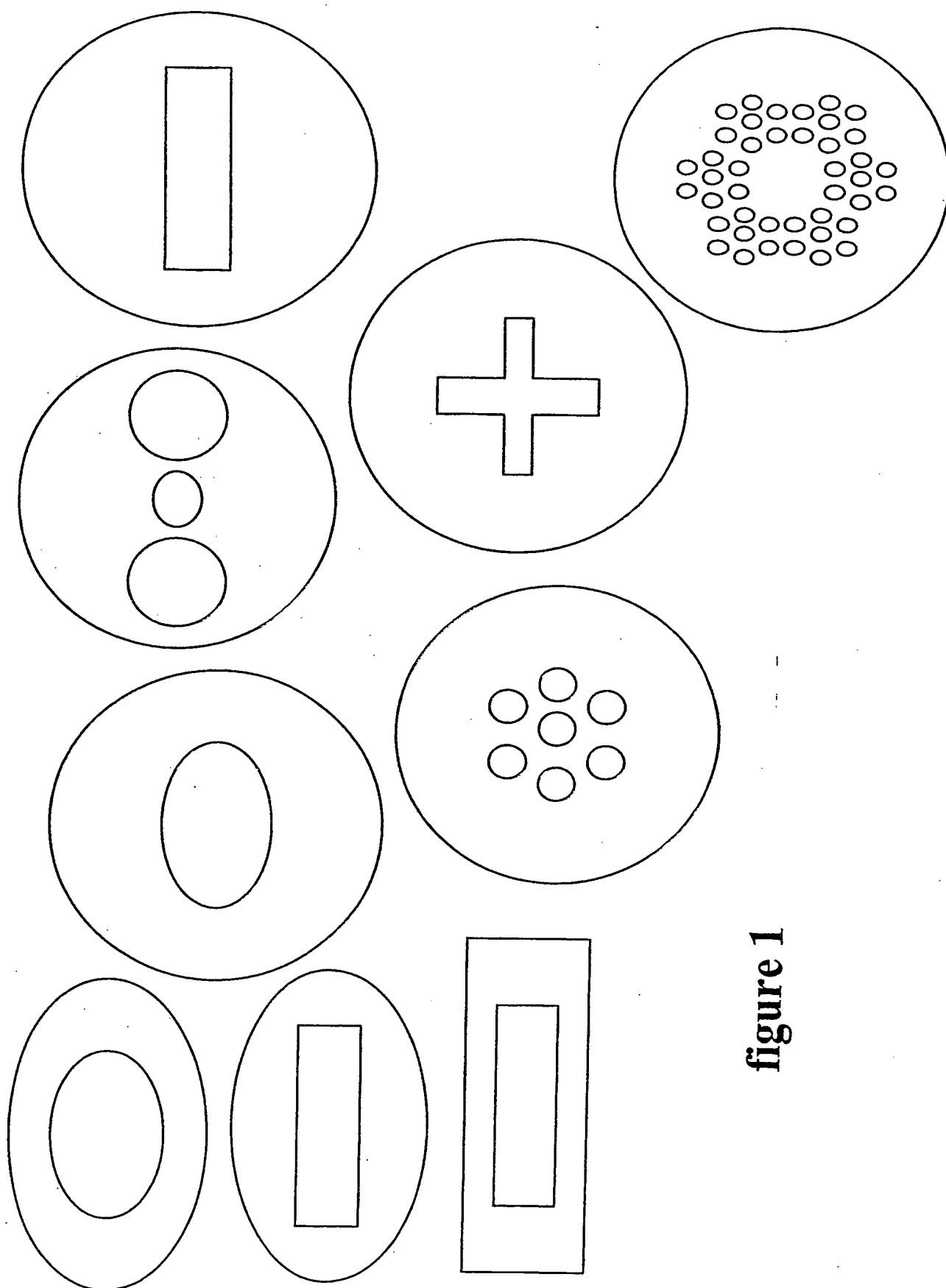


figure 1

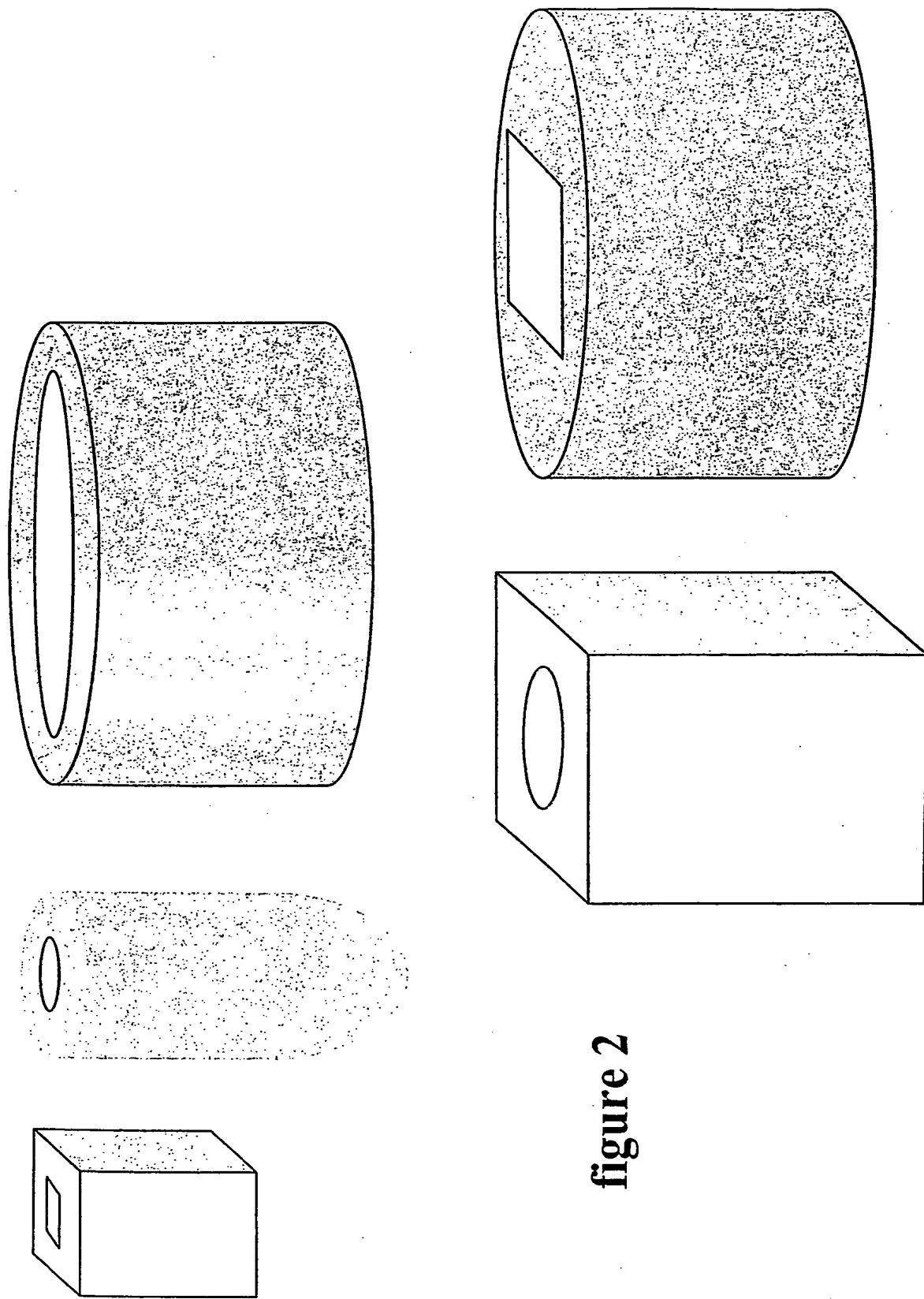


figure 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/002578

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03B19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
| X | WO 00/53536 A (NOVARA TECHNOLOGY S R L ; COSTA LORENZO (IT); COSTA FULVIO (IT); COSTA) 14 September 2000 (2000-09-14) | 1,2,4 |
| Y | abstract example 1 | 3,4 |
| Y | EP 1 172 339 A (LUCENT TECHNOLOGIES INC) 16 January 2002 (2002-01-16) abstract; figure 5 | 3. |
| Y | PATENT ABSTRACTS OF JAPAN vol. 2003, no. 02, 5 February 2003 (2003-02-05) -& JP 2002 293548 A (FURUKAWA ELECTRIC CO LTD:THE; YOSHIDA KAZUAKI), 9 October 2002 (2002-10-09) abstract; figure 2 | 3 |
| | -/- | |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

10 June 2004

Date of mailing of the international search report

21/06/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Picard, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/002578

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| Y | PATENT ABSTRACTS OF JAPAN vol. 0103, no. 66 (C-390), 6 December 1986 (1986-12-06) & JP 61 163131 A (SEIKO EPSON CORP), 23 July 1986 (1986-07-23) abstract ----- | 4 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/002578

| Patent document cited in search report | | Publication date | | Patent family member(s) | | Publication date |
|--|---|------------------|--|---|--|--|
| WO 0053536 | A | 14-09-2000 | | IT N0990004 A1 AT 254091 T AU 759015 B2 AU 3323800 A BR 0008692 A CA 2366247 A1 CN 1343184 T DE 60006517 D1 EP 1175377 A1 WO 0053536 A1 JP 2003513873 T | | 08-09-2000 15-11-2003 03-04-2003 28-09-2000 26-12-2001 14-09-2000 03-04-2002 18-12-2003 30-01-2002 14-09-2000 15-04-2003 |
| EP 1172339 | A | 16-01-2002 | | US 6467312 B1 DE 60100159 D1 DE 60100159 T2 EP 1172339 A1 JP 2002068771 A | | 22-10-2002 08-05-2003 04-03-2004 16-01-2002 08-03-2002 |
| JP 2002293548 | A | 09-10-2002 | | NONE | | |
| JP 61163131 | A | 23-07-1986 | | NONE | | |